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Iron-Promoted Practical One-Pot Synthesis of 2,5-Disubstituted Oxazoles

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A practical one-pot protocol for the synthesis of 2,5-disubstituted oxazoles from 1-aryl-2-nitroethanones was reported. In the presence of iron/AcOH in acetonitrile, the reaction of 1-aryl-2-nitroethanones with trimethyl orthoacetate or trimethyl orthobenzoate delivered the corresponding 2,5-disubstituted oxazoles in moderate to good yields.

Keywords oxazole, iron, one pot synthesis

Introduction

Oxazoles occur widely in numerous natural products, and are an important class of heterocycle that exhibit various biological activities such as antihypertensive, anticancer, antiulcer, anti-inflammatory agents, fungicides, and adrenergic antagonists.[1] Many compounds containing an oxazole structural unit are also used as versatile synthetic intermediates in organic synthesis.[2] Thus, much attention[3] has been devoted to the development of new and efficient methods for the synthesis of oxazole derivatives. The cyclodehydration of the α-acylamino ketones (Robinson-Gabriel reaction)[4] and the oxidation of oxazolines represent direct approaches in literature precedents.[5,3b]

Recently, an indium-mediated one-pot synthesis of 2,5-disubstituted oxazoles from the reaction of 1-aryl-2-nitroethanones and trimethyl orthobenzoate or trimethyl orthoacetate has been reported.[6] However, this method was not economical and practical as indium metal is expensive. In addition, only an example was explored on the reactivity of trimethyl orthoacetate to result in the poor yield of 2-methyl-5-phenyloxazole. As a continuation on the syntheses of carbocycles and potentially bioactive heterocycles as well as the organic synthetic reactions mediated by metal,[7] we wish to report here a practical and economic one-pot synthesis of 2,5-disubstituted oxazoles from the reaction of 1-aryl-2-nitroethanones with trimethyl orthoacetate, or trimethyl orthobenzoate using cheap iron powder as promoter.

Results and Discussion

In an effort to develop a better reaction system, our initial experiment was carried out by using 1-phenyl-2-nitroethanone and trimethyl orthoacetate as model substrate (Eq. 1). Firstly, we investigated the direct transformation of 1-phenyl-2-nitroethanone and trimethyl orthoacetate with metallic samarium in the absence of any additive in acetonitrile as a solvent. No reaction occurred when 1-phenyl-2-nitroethanone and trimethyl orthoacetate were mixed with samarium powder in acetonitrile (Table, Entries 1). Fortunately, 10% yield of 2-methyl-5-phenyloxazole was isolated when the reaction was carried out in the presence of acetic acid (Table 1, Entry 2). Subsequently, a few molecular iodines or titanium(IV) chloride were then added to activate the metallic samarium powder to afford lower yields of product (Table 1, Entries 3, 4). Similar results were observed under the same reaction conditions when zinc was used as a reducing agent (Table 1, Entries 5—7). To our delight, applying iron powder to this system brought great improvement. As can be seen from Table 1, in the presence of iron powder and acetic acid, 2-methyl-5-phenyloxazole was obtained in 50% yield (Table 1, Entry 8). While the titanium(IV) chloride or iodine was employed, 2-methyl-5-phenyloxazole was obtained in 40% and 21% yields, respectively (Table 1, Entries 9, 10). Moreover, the increase or reduction of acetic acid dosage also resulted in low yields (Table 1, Entries 11, 12). Then we investigated the effect of different solvents on this reaction. The experimental results indicated that when 1,4-dioxane, THF, toluene, or DCM

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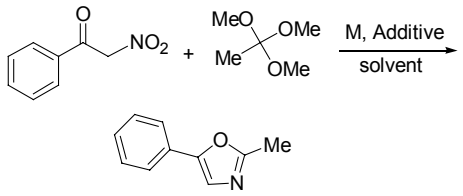
† With equal contribution to this work.

was used as solvent respectively, low yields of the product were afforded (Table 1, Entries 13—16). On the other hand, the product conversion was susceptible to temperature change. The decrease of reaction temperature to 25 ℃ led to long reaction time and low yield (Table 1, Entry 17). Therefore, the best result was obtained when the reaction of 1-phenyl-2-nitroethanones (0.5 mmol) with trimethyl orthoacetate (2.0 mmol) was carried out in the presence of iron powder (2.0 mmol), AcOH (5.0 mmol) using acetonitrile as solvent at reflux (Table 1, Entry 8).



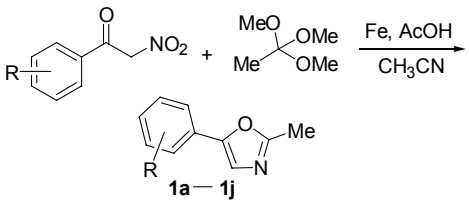
(1)

Table 1 Optimization of reaction condition[a]

Entry	M	Solvent	Additive	Time/h	Yield[b]/%
1	Sm	CH_3CN	—	4	0
2	Sm	CH_3CN	AcOH	4	10
3	Sm	CH_3CN	Iodine	4	3
4	Sm	CH_3CN	$TiCl_4$	4	8
5	Zn	CH_3CN	AcOH	4	30
6	Zn	CH_3CN	Iodine	4	18
7	Zn	CH_3CN	$TiCl_4$	4	15
8	Fe	CH_3CN	AcOH	4	50
9	Fe	CH_3CN	I_2	4	21
10	Fe	CH_3CN	$TiCl_4$	4	40
11	Fe	CH_3CN	AcOH[c]	10	30
12	Fe	CH_3CN	AcOH[d]	10	28
13	Fe	1,4-dioxane	AcOH	6	27
14	Fe	THF	AcOH	5	26
15	Fe	toluene	AcOH	5	35
16	F	DCM	AcOH	5	19
17	Fe	CH_3CN	AcOH	24	30[e]

[a] Reaction conditions: 1-phenyl-2-nitroethanone (0.5 mmol), trimethyl orthoacetate (2 mmol), solvent (15 mL), M (2 mmol), additive (5 mmol) reflux. [b] Isolated yields. [c] AcOH (8 mmol). [d] AcOH (3 mmol). [e] Room temperature.

We then focused on our attention to substrate generality using the optimized reaction conditions. The reaction of various 1-aryl-2-nitroethanones with trimethyl orthoacetate was examined (Eq. 2) and the results were summarized in Table 2. As can be seen from Table 2, the reaction of various 1-aryl-2-nitroethanones having electron-neutral, electron-deficient, and electron-rich substituent groups on the aromatic ring with trimethyl orthoacetate was performed well to provide the corresponding 2-methyl-5-aryloxazoles in moderate to good yields (Table 2), and no obvious sterical hindrance effect was observed in all cases (Table 2). In addition, bromo, chloro, fluoro, methoxy and methyl group substitution on the aromatic ring were all tolerated, which were potentially useful for further functionalization.

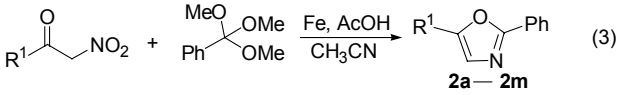


1a— **1j** (2)

Table 2 Synthesis of various 2-methyl-5-aryloxazoles [a]

Entry	R	Time/h	Yield[b]/%
1	H	4	50 (**1a**)
2	*o*-CH_3	6	52 (**1b**)
3	*m*-CH_3	8	70 (**1c**)
4	*p*-CH_3	13	65 (**1d**)
5	*o*-OCH_3	11	65 (**1e**)
6	*m*-OCH_3	8	75 (**1f**)
7	*o*-Cl	10	47 (**1g**)
8	*p*-Cl	5	63 (**1h**)
9	*p*-F	9	59 (**1i**)
10	*m*-Br	4.5	49 (**1j**)

[a] Reaction conditions: 1-aryl-2-nitroethanone (0.5 mmol), trimethyl orthoacetate (2 mmol), acetonitrile (15 mL), reflux. [b] Isolated yields.



2a— **2m** (3)

Finally, the reaction of 1-aryl-2-nitroethanones with trimethyl orthobenzoate was tested using the same reaction condition (Scheme 3) and the results were summarized in Table 3. In all cases, 1-aryl-2-nitroethanones

Table 3 Synthesis of various 2,5-diaryloxazoles[a]

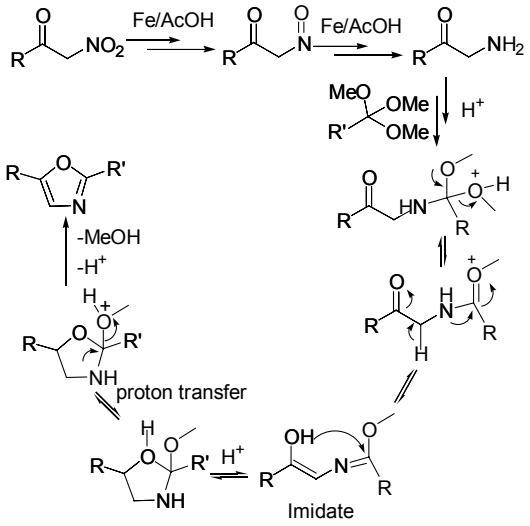
Entry	R^1	Time/h	Yield[b]/%
1	C_6H_5	3.5	72 (**2a**)
2	*o*-$CH_3C_6H_4$	6	50 (**2b**)
3	*m*-$CH_3C_6H_4$	5	77 (**2c**)
4	*p*-$CH_3C_6H_4$	18	80 (**2d**)
5	*o*-$CH_3OC_6H_4$	9	54 (**2e**)
6	*m*-$CH_3OC_6H_4$	11	62 (**2f**)
7	*p*-$CH_3OC_6H_4$	3.5	46 (**2g**)
8	*o*-ClC_6H_4	3.75	62 (**2h**)
9	*m*-ClC_6H_4	14	65 (**2i**)
10	*p*-ClC_6H_4	5	68 (**2j**)
11	*p*-FC_6H_4	13	60 (**2k**)
12	*m*-BrC_6H_4	11.5	61 (**2l**)
13	furan-2-yl	5	50 (**2m**)

[a] Reaction conditions: 1-aryl-2-nitroethanone (0.5 mmol), trimethyl orthobenzoate (2 mmol), acetonitrile (15 mL), reflux. [b] Isolated yields.

bearing both electron-withdrawing and electron-donating groups on aromatic rings underwent smooth transformation to the corresponding 2,5-diaryloxazoles in moderate to good yields (Table 3).

A possible mechanism is proposed in Eq. 4. By the consequent electron transfers and proton transfers, the nitro group could first transform into a nitroso intermediate. The nitroso intermediate may be converted into the amine species by electron transfer and proton transfer processes as well as the change of ketone to enol, and then it can react further to the imidate intermediate. Next, an acid-assisted attack by the hydroxyl group toward the neighboring imidate group followed by the loss of MeOH and proton would produce oxazoles.

Scheme 4



Conclusions

In conclusion, we have developed a facile, practical and economic one-pot method for the synthesis of 2,5-disubstituted oxazoles from 1-aryl-2-nitroethanones. In the presence of iron/AcOH, the reaction of 1-aryl-2-nitroethanones with trimethyl orthoacetate, or trimethyl orthobenzoate gave the corresponding 2,5-disubstituted oxazoles in moderate to good yields. The great attractiveness of the current method lies in simple experimental procedure, use of cheap iron powder, especially, the development of reaction of 1-aryl-2-nitroethanones with trimethyl orthoacetate to 2-methyl-5-aryloxazoles. These features make this methodology economical, facile and practical for use in medicinal and synthetic chemistry.

Experimental

All reagents and solvents were obtained from commercial sources and used without purification, unless indicated otherwise. Nitro ketones were prepared according to reported method.[8] NMR spectra were recorded on a Bruker DRX-500 NMR spectrometer (500 MHz for ^{1}H and 125 MHz for ^{13}C) with $CDCl_3$ as the solvent and TMS as internal reference. Coupling constants (J) are reported in Hz. High-resolution mass spectra (HRMS) were recorded on an IonSpec 4.7 Tesla FTMS instrument.

General procedure

The suspension of iron powder (2 mmol), 1-aryl-2-nitroethanones (0.5 mmol) and acetic acid (5 mmol) in CH_3CN (5 mL) was stirred for 5 min at room temperature under a nitrogen atmosphere. And then trimethyl orthoacetate, or trimethyl orthobenzoate in acetonitrile (10 mL) was added. The reaction mixture was allowed to react at reflux. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was filtered and the solid was washed with dichloromethane. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate to afford the corresponding 2,5-disubstituted oxazoles in moderate to good yields. All the compounds reported were identified by melting points, ^{1}H NMR and ^{13}C NMR spectra. The new compounds were identified by HRMS.

2-Methyl-5-phenyloxazole (1a) White solid, m.p. 55—57 ℃ (lit.[9] 57—58 ℃); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.61—7.28 (m, 5H), 7.19 (s, 1H), 2.52 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 161.1, 151.2, 128.9, 128.3, 128.2, 124.0, 121.9, 14.2.

2-Methyl-5-(*o*-tolyl)oxazole (1b) Colorless liquid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.66 (d, J=7.0 Hz, 1H), 7.28—7.22 (m, 3H), 7.10 (s, 1H), 2.53 (s, 3H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 160.8, 150.5, 134.7, 131.2, 128.2, 127.5, 126.6, 126.2, 124.8, 21.9, 14.1; HRMS calcd for $C_{11}H_{11}NO$ $[M+H]^+$ 174.0913, found 174.0919.

2-Methyl-5-(*m*-tolyl)oxazole (1c) Colorless liquid;[10] ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.41—7.25 (m, 3H), 7.18 (s, 1H), 7.10 (d, J=7.5 Hz, 1H), 2.51 (s, 3H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 167.4, 151.3, 138.5, 128.9, 128.8, 128.7, 128.1, 124.5, 121.7, 121.1, 21.4, 14.1.

2-Methyl-5-(*p*-tolyl)oxazole (1d) Light yellow solid, m.p. 55—56.8 ℃ (lit.[10] 56—57 ℃); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.49 (d, J=8.5 Hz, 2H), 7.20 (d, J=8.5 Hz, 2H), 7.16 (s, 1H), 2.53 (s, 3H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 161.0, 151.5, 138.3, 129.6, 129.4, 128.4, 125.4, 124.1, 121.1, 21.4, 14.2.

2-Methyl-5-(*o*-methoxyphenyl)oxazole (1e) Light yellow solid, m.p. 57.8—60.2 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.73 (dd, J=9.5, 1.5 Hz, 1H), 7.28 (s, 1H), 7.27—6.94 (m, 3H), 3.93 (s, 3H), 2.52 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 155.4, 128.7, 126.1, 125.6, 120.8, 117.4, 110.8, 55.4, 14.1. HRMS calcd for $C_{11}H_{11}NO_2$ $[M+Na]^+$ 212.0682, found 212.0687.

2-Methyl-5-(*m*-methoxyphenyl)oxazole (1f) Colorless liquid;[10] ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.31—7.18 (m, 2H), 7.13 (s, 1H), 6.85—6.83 (m, 1H), 3.84 (s, 3H), 2.53 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ:

159.9, 130.0, 129.4, 122.2, 120.8, 116.5, 113.9, 112.3, 109.3, 55.3, 14.1.

2-Methyl-5-(*o*-chlorophenyl)oxazole (1g) Colorless liquid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.77 (d, J=7.5 Hz, 1H), 7.64 (s, 1H), 7.45—7.27 (m, 2H), 7.22 (t, J=7.5 Hz, 1H), 2.54 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 161.0, 147.7, 130.7, 130.4, 128.7, 127.5, 127.1, 127.0, 126.9, 14.1; HRMS calcd for $C_{10}H_8ClNO$ $[M+Na]^+$ 216.0186, found 216.0190.

2-Methyl-5-(p-chlorophenyl)oxazole (1h) White solid, m.p. 73—74.5 ℃ (lit.[11] 74—75.5 ℃); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.51 (d, J=8.5 Hz, 2H), 7.35 (d, J=8.5 Hz, 2H), 7.18 (s, 1H), 2.51 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 161.4, 150.2, 133.9, 129.2, 126.7, 125.2, 122.4, 14.2.

2-Methyl-5-(*p*-fluorophenyl)oxazole (1i) Light yellow solid, m.p. 51.5—53.4 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.56—7.53 (m, 2H), 7.12 (s, 1H), 7.11—7.06 (m, 2H), 2.49 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 163.5, 161.5, 161.1, 150.4, 125.9, 125.8, 124.6, 124.5, 121.5, 116.1, 115.9, 14.1; HRMS calcd for $C_{10}H_8FNO$ $[M+Na]^+$ 177.0590, found 177.0591.

2-Methyl-5-(*m*-bromophenyl)oxazole (1j) Colorless liquid;[10] ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.75 (s, 1H), 7.74—7.22 (m, 4H), 2.53 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 161.7, 149.8, 131.1, 130.5, 130.1, 126.9, 123.1, 122.8, 122.5, 14.2.

2,5-Diphenyloxazole (2a) White solid, m.p. 74.5—76.2 ℃ (lit.[6] 75—77 ℃); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.12 (d, J=8.0 Hz, 2H), 7.73 (d, J=7.5 Hz, 2H), 7.50—7.33 (m, 7H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 161.3, 151.4, 130.5, 129.1, 128.9, 128.6, 128.1, 127.6, 126.4, 124.3, 123.6.

2-Phenyl-5-(*o*-tolyl)oxazole (2b) White solid, m.p. 72—73.8 ℃ (lit.[6] 72—74 ℃); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.11—7.23 (m, 10H), 2.51 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 160.8, 150.8, 134.9, 131.3, 130.4, 128.9, 128.4, 127.5, 127.3, 126.8, 126.4, 126.3, 126.2, 22.0.

2-Phenyl-5-(*m*-tolyl)oxazole (2c) White solid, m.p. 119—120.5 ℃ (lit.[6] 120—121 ℃); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.12 (dd, J=9.5, 1.5 Hz, 2H), 7.54—7.15 (m, 8H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 161.2, 151.5, 138.8, 130.4, 129.4, 129.0, 128.9, 128.0, 127.6, 126.4, 124.9, 123.5, 121.5, 21.6.

2-Phenyl-5-(*p*-tolyl)oxazole (2d) White solid, m.p. 83.8—85 ℃ (lit.[6] 85—86 ℃); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.11—8.10 (m, 2H), 7.60 (d, J=8.0 Hz, 2H), 7.49—7.44 (m, 3H), 7.40 (s, 1H), 7.23 (d, J=7.5 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MH_z) δ: 160.8, 151.5, 138.5, 130.2, 129.6, 128.8, 127.6, 126.3, 125.3, 124.2, 122.8, 21.4.

2-Phenyl-5-(*o*-methoxyphenyl)oxazole (2e) White solid, m.p. 126—128 ℃ (lit.[6] 129—131 ℃); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.15—8.12 (m, 2H), 7.90 (dd, J=7.5, 1.5 Hz, 1H), 7.65 (s, 1H), 7.53—6.96 (m, 6H), 3.98 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 160.1, 155.8, 147.9, 130.3, 129.2, 128.9, 127.7, 126.4, 125.9, 120.9, 120.2, 117.3, 111.0, 55.6.

2-Phenyl-5-(*m*-methoxyphenyl)oxazole (2f) White solid, m.p. 96—98 ℃ (lit.[6] 97—98 ℃); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.09 (d, J=7.0 Hz, 2H), 7.48—7.23 (m, 7H), 6.87 (d, J=7.5 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 160.0, 151.2, 130.4, 130.1, 129.3, 128.9, 127.4, 126.3, 123.8, 116.8, 109.8, 55.4.

2-Phenyl-5-(*p*-methoxyphenyl)oxazole (2g) White solid, m.p. 85—88 ℃ (lit.[6] 88—89 ℃); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.10 (dt, J=7.0, 1.5 Hz, 2H), 7.64 (t, J=8.5 Hz, 2H), 7.49—7.42 (m, 3H), 7.32 (s, 1H), 6.96 (d, J=9.0 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 160.6, 159.9, 151.4, 130.2, 128.8, 127.6, 126.2, 125.8, 122.0, 120.9, 114.4, 55.4.

2-Phenyl-5-(*o*-chlorophenyl)oxazole (2h) White solid, m.p. 78.7—80.2 ℃ (lit.[6] 79—80 ℃); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.11 (dt, J=4.0, 1.5 Hz, 2H), 7.88—7.34 (m, 8H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 161.0, 147.8, 130.8, 130.6, 128.9, 128.9, 128.5, 128.1, 127.6, 127.2, 127.1, 126.8, 126.5.

2-Phenyl-5-(*m*-chlorophenyl)oxazole (2i) White solid, m.p. 118—119.5 ℃ (lit.[6] 119—120 ℃); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.13 (dt, J=3.5, 3.0 Hz, 2H), 7.71 (s, 1H), 7.61—7.32 (m, 7H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 161.7, 150.3, 135.3, 131.4, 130.5, 129.3, 129.2, 128.9, 126.8, 126.3, 124.4, 123.3, 122.5.

2-Phenyl-5-(*p*-chlorophenyl)oxazole (2j) White solid, m.p. 106—108 ℃ (lit.[6] 110—111 ℃); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.10—8.08 (m, 2H), 7.63 (d, J=8.5 Hz, 2H), 7.48—7.39 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 161.3, 150.4, 134.3, 130.6, 129.3, 128.9, 127.3, 126.6, 126.4, 125.5, 123.9.

2-Phenyl-5-(*p*-fluorophenyl)oxazole (2k) White solid, m.p. 100—102 ℃ (lit.[6] 101—103 ℃); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.10—7.44 (m, 7H), 7.38 (s, 1H), 7.16—7.12 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 163.8, 161.6, 161.2, 150.5, 130.5, 128.9, 127.4, 126.4, 126.2, 126.2, 124.5, 124.4, 123.2, 116.3, 116.1.

2-Phenyl-5-(*m*-bromophenyl)oxazole (2l) White solid, m.p. 115—116.9 ℃ (lit.[6] 116—117 ℃); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.17—8.07 (m, 2H), 7.87 (s, 1H), 7.64 (d, J=7.78 Hz, 1H), 7.51—7.44 (m, 5H), 7.31 (t, J=7.89 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 161.8, 149.8, 131.4, 130.7, 130.6, 130.0, 129.0, 127.1, 126.5, 124.5, 123.2, 122.8.

2-Phenyl-5-(furan-2-yl)oxazole (2m) White solid, m.p. 71.5—73.2 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.08—8.07 (m, 2H), 7.47—7.41 (m, 4H), 7.35 (s, 1H), 6.68 (d, J=3.50 Hz, 1H), 6.50—6.48 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 160.8, 143.8, 143.7, 142.9, 133.0, 130.5, 129.6, 128.9, 128.4, 127.2, 126.4, 123.4, 111.7, 107.4; HRMS calcd for $C_{13}H_9NO_2$ $[M+Na]^+$ 234.0525, found 234.0529.

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